

Relaxation of Photoexcited Electron-Hole Pairs at Si(111) Surfaces with Adsorbed Ag Cluster Monolayers

Yulun Han[†], Tijo Vazhappilly[‡], David A. Micha[§], Dmitri S. Kilin[†]

[†]*Department of Chemistry and Biochemistry, North Dakota State University, Fargo, North Dakota 58102, USA*

[‡]*Theoretical Chemistry Section, Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India and Homi Bhabha National Institute, Mumbai 400094, India*

[§]*Quantum Theory Project, Departments of Chemistry and of Physics, University of Florida, Gainesville, Florida 32611, USA*

Optoelectronic properties of semiconducting nanostructures have attracted much attention due to their applications in photovoltaics and photocatalysis. Transition metal nanoclusters show fascinating optical and chemical properties that depend on the size, shape, and composition of the clusters. Deposition of transition metal clusters onto semiconductor surfaces leads to stronger absorption of light and additional pathways for charge transfer compared to pure surfaces. In this work, we study relaxation dynamics of electron-hole pairs following photoexcitations for various Ag_n (n=0, 3, 7 and 10) cluster monolayers adsorbed on Si(111)/H surfaces. We first carry out density functional theory (DFT) calculations to obtain electronic structures. Results are presented in the form of density of states, band gaps, and light absorption, which allow for the investigation of the interaction of Ag clusters with Si. Different behavior can be expected depending on the size of the deposited Ag clusters. We then compute dynamics of electron-hole pairs using the combined electronic structure and reduced density matrix (RDM) treatment.¹⁻³ Specifically, we compute on-the-fly nonadiabatic couplings from DFT and process them using the RDM approach within the Redfield formalism. Nonradiative relaxation rates are noticeably different for various structures and transitions. One observes smaller relaxation rates for surfaces with adsorbates than pure Si surfaces due to charge transfer events with the contribution of Ag orbitals. Thus, introduction of adsorbates is advantageous for applications to photovoltaics and photocatalysis.

This work has been partly supported by NSF CHE-1944921. DAM thanks recent support from the NSF CHE Division and from the University of Florida computing center.

References

1. D. S. Kilin, D. A. Micha. Surface Photovoltage at Nanostructures on Si Surfaces: Ab Initio Results. *J. Phys. Chem. C* 2009, 113, 9, 3530-3542.
2. D. S. Kilin, D. A. Micha. Relaxation of Photoexcited Electrons at a Nanostructured Si(111) Surface. *J. Phys. Chem. Lett.* 2010, 1, 7, 1073-1077.
3. T. Vazhappilly, Y. Han, D. S. Kilin, D. A. Micha. Electronic Relaxation of Photoexcited Open and Closed Shell Adsorbates on Semiconductors: Ag and Ag₂ on TiO₂. *J. Chem. Phys.* 2022, 156, 10, 104705.